

molecular motions become apparent. It is only above 40°C that rapid polymerization occurs, and in this temperature range a very narrow line is present in the centre of the n.m.r. spectrum, corresponding to considerable molecular motion. From theoretical calculations of second moments, Komaki and Matsumoto interpret the motions present at about 25°C as chair-chair interconversions, occurring by the proton pairs undergoing a sinusoidal oscillation about the axis perpendicular to the pair direction.⁽¹³⁹⁾ At about 45°C the movements are interpreted as chair-chair interconversions by rotation of the whole molecule about its C_3 -axis, with the narrow line being attributed to a fraction of the molecules adopting a boat conformation and rotating about the axis perpendicular to the ring plane.⁽¹³⁹⁾ Obviously, there is considerable molecular movement near the melting point (trioxan is a well-known example of a plastic crystal) and it might be expected that diffusion of small molecules through the lattice could occur easily at these temperatures. It is now known that at least some of the decrease in rate of polymerization as the crystal melts is caused by the presence of impurities, and the decrease in rate as the melting point is approached could be at least partly due to diffusion of impurities (e.g. water) which terminate the polymerization, especially since polymerizations are usually carried out in the air. (The addition of water in quantities greater than 0.01 per cent does reduce rates of polymerization.⁽¹³¹⁾)

Although polymerization of these monomers by a ring opening mechanism does not require the formation of any new bond types, a certain amount of molecular rearrangement is required for polymerization. Carazzolo *et al.*⁽¹²²⁾ found that polyoxymethylene formed during the solid-state polymerization of trioxan crystallizes as a helix with 1.81—CH₂—O—units per turn, whereas the monomer has 3 units per ring. The formation of polymer, therefore, requires that the ends of an open ring overlap, causing a contraction in the *a* and *b* directions and some further rearrangement in the *c* direction. These rearrangements are presumably facilitated by the high molecular mobility under the polymerization conditions.

In view of the high molecular mobility and necessary rearrangements it might be thought surprising that highly orientated polymers are formed during the polymerization of a monomer such as trioxan. Adler has demonstrated that the influence of the lattice is not as important as was first visualized by studying the post-polymerization using polycrystalline samples (in the form of thin layers of single crystals) instead of a large single crystal.⁽⁴⁰⁾ Irradiation of samples at 24°C and storage at the same temperature gave small amounts of crystalline fibrous polymer on the crystal surfaces; these fibres exhibited no preferred direction with respect to monomer crystal axes. Indeed, some fibres even changed direction. When the post-irradiation polymerization was carried out at 46°C there was extensive polymerization and the bundles of crystalline polymer fibres grew across intercrystalline boundaries, with little or no change in direction, although the crystals through which the

polymer forms showed different orientations. The bundles of fibres were also observed to extend beyond crystal boundaries and grow through the space between individual crystals.⁽⁴⁰⁾ It must be concluded from the results at these two temperatures that the growth of crystalline polymer does not require a specific orientation of monomer. As a result of post-irradiation polymerization at 54°C the polymer fibres were found to be aligned, almost exclusively, parallel to the *c*-axis of the monomer crystals. However, there had been extensive recrystallization of the samples during reaction. The monomer crystals which then surrounded the crystalline polymer were larger and fewer in number than in the original sample. These results are reconciled with the older results, where all the polymer formed during the polymerization of single crystals was aligned along preferred directions in the monomer crystal, by assuming that polymer is initially formed in a preferred direction;⁽⁴⁰⁾ subsequently growth is then controlled by addition of monomer to polymer which has crystallized in the form of a helix. Thus it is the crystallizability of the polymer which controls the nature of the product, rather than the crystal structure of the monomer. Adler also reports similar behaviour in the polymerization of trithiane.⁽⁴⁰⁾ Lando and Stannett⁽¹²³⁾ find that the n.m.r. line width in trithiane shows little change in the temperature range 25°–180°C, although post-irradiation polymerization is observed at 180°C and not at 150°C.

The fact that polymer, formed in single crystals of monomer, is always orientated along a preferred direction, suggests that polymerization is initiated at a specific type of lattice site, presumably a specific imperfection, and that it is the nature of this imperfection which determines the manner in which polymer is initially laid down in the monomer lattice. Very recently, Bassett⁽¹⁴⁰⁾ has obtained photomicrographic evidence that the {00·1} sub-grain boundaries are these specific sites at which polymerization commences.

It is notable that the only monomers which polymerize in the solid state to give crystalline polymers directly are those which give rise to readily crystallizable polymers. All the polymers which have so far been produced in a crystalline form have a symmetrical structure with no asymmetric carbon atoms in the backbone. Solid-state polymerization of hexamethyltrisiloxane gives an amorphous polymer, and it may be noted that this polymer is less easily crystallizable than those which are produced in the crystalline form.

Nature of the Reactive Species

Free radicals have been detected in some γ -irradiated cyclic monomers. γ -irradiation of trioxan at -196°C gives an anisotropic e.s.r. spectrum together with an isotropic doublet attributed to the formyl radical; subsequent exposure to u.v. radiation is reported to increase the concentration of the formyl radicals and exposure to light of wavelength $> 2800 \text{ \AA}$ to decrease